PROJECT NUMBER: 6505
PROJECT TITLE: Special Investigations/Methods Development
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I. METHODS FOR CASINGS AND AFTERCUTS

A. Objective: To develop rapid methods for the quantitation of propylene glycol, glycerin, ethanol, water, and isosweet in casings and aftercuts.

B. Results:

Sugars in bright casing appear to break down in the injection port causing a build-up of potential interferences on the Porapak® PS column. More than four hundred injections of dilute bright casing were made on a PS column to test its durability. A slight decrease in peak resolution and baseline stability was observed after about two hundred injections, but the column was returned to an acceptable performance level by heating the oven to 225°C for two hours.

Ethylene glycol (EG) was identified as an acceptable internal standard for this method. EG is automatically dispensed into standard and sample flasks using a Unipump 300. The pump dispenses EG with a relative precision of ± 0.2% (2-sigma) as measured by weight. EG cannot be added directly to the diluent because of a dilution effect when preparing the concentrated stock standard.

Several changes were made in the method to improve peak resolution and decrease total run time. An increase in column length (3' to 4') and a change in diluent (methanol to n-propanol) improved the resolution of water and the solvent front permitting the use of a higher initial temperature (125°C versus 85°C). The total run time was thereby reduced by three minutes. In addition, the sugars in the bright casing are sparingly soluble in n-propanol which reduces the presence of associated background interferences.

Four unknown casings (top and bright) were supplied by E. Tucker for analysis. Good agreement was observed between the measured concentrations of water, ethanol, PG, and glycerin and the calculated concentrations based on preparation. Relative standard deviations (2-sigma) for a typical bright casing were determined to be ± 4% for water, ± 1% for propylene glycol, and ± 3% for glycerin.

C. Plans: 1) To complete recovery studies, 2) to determine the relative standard deviation for a typical top casing, 3) to evaluate the method for aftercuts and burley spray, and 4) to present the method to the QA Methods committee on August 2nd.

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II. SPECIFICATIONS AND ANALYSIS OF INCOMING BULK LIQUIDS

A. **Objective**: To evaluate the specifications and analytical testing protocol for bulk shipments of propylene glycol, glycerin, isosweet, and ethanol (SD-4).

B. **Status**: Discussions with Quality Assurance personnel were completed. The information was collated onto spreadsheets and reviewed for accuracy by the respective facilities. Recommendations for the analytical testing protocol were prepared in collaboration with C. Kroustalis and M. Zimmermann.

C. **Plans**: To issue the recommendations and corresponding test procedures to J. Crichton for distribution to the QA facilities. Following, a meeting will be held with personnel from all locations to discuss these recommendations.

III. PROJECT ART

A. **Objective**: Provide analytical support to project ART.

B. **Results**:

Support for project ART fell into two areas. Richard Davis assumed responsibility for the ART pilot facility laboratory for two weeks. Operation of the lab was essentially uneventful although some suggestions were made to improve lab operation.

The second area was the program to provide a viable online nicotine monitor. Three alternatives are under consideration exclusive of the HPLC monitor now in place in the ART pilot facility. A GC centered device is under study by Applied Automation with the goal of a vendor supported, turnkey system. The second is the determination of nicotine online by uv spectroscopy. The third is the use of circular dichroism spectroscopy (CD) as an online tool. The uv study will await the termination of the CD study and the procurement of a suitable uv spectrometer. The CD study is in progress following the purchase and installation of a Jasco J-600 CD spectrophotometer. The unit was interfaced with a supercritical microextractor fitted with a flow-through 1-cm optical cell. Initial results have been encouraging. Sources of spectral noise have been traced to thermal gradients of the supercritical CO2 within the optical cell. Heat tracing of the inlet line reduced the noise to an acceptable level. A preliminary standard curve generated within the microextractor system proved linear and time scans of an initial extraction of a previously extracted DL blend resulted in calculated values which gave acceptable agreement with offline sampling and nicotine determination by GC.

C. **Conclusions**: The online CD determination of nicotine shows promise as a viable technique with acceptable sensitivity and selectivity.

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D. **Plans**: Monitoring of Applied Automation's progress will continue with a target date of August 26, 1988 for submission of their results. The uv study will await the inhouse demonstration of a uv instrument by Chrom-A-Scope. Studies of the CD technique will continue with an actual extraction absorption run of AB sprayed DL filler in the microextractor using potassium citrate sprayed CRS. Following this will be an attempt to measure the process stream using a stopped flow technique which should result in less background noise in the CD signal.

E. **References**:

Davis, R. E., "ART Online Process Nicotine Monitor - Progress Report," memo to R. Cox, July 11, 1988.

IV. ANALYSIS OF RESIDUAL SOLVENTS IN PACKAGING MATERIALS

A. **Objective**: To provide headspace analyses for residual solvents from packaging materials and develop a QA method for the routine analysis of packaging materials.

B. **Results**: A method has been written and is awaiting approval for the headspace/gas chromatographic analysis of solvents in packaging materials. Samples have been analyzed over the past month for Flavor Development. The printers are switching to solvents that we have not encountered previously. Several of these compounds have been identified by FT-IR and GC/FT-IR/MS. One compound tentatively identified as butyl cellosolve is being detected on a regular basis. The compound has been ordered so that we can positively identify and quantitate it.

C. **Plans**: Compare the performance of QA's set-up to ours. QA will take over the responsibility for these analyses once they can obtain good quality, consistent results.

V. UNEXTRACTED NICOTINE

A. **Objective**: To quantitate and characterize unextracted nicotine.

B. **Results**:

The effect of water content on the extraction of nicotine by methanol/ammonia was investigated. Results showed that the longer the equilibration time after addition of water, the more efficient the extraction of nicotine is. Additionally, the longer the extraction time, the more nicotine that is extracted, over a 24 hour period. The effect of extraction time is less important at higher OV's (above 20%), however. On a relative basis, these effects are more significant for ART extracted tobacco (~ 0.07% nicotine) than on unextracted filler.

Samples prepared by W. Hempfling were also analyzed for nicotine in support of this project. At this point, treatment of ART

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filler with hot, 1 N sodium hydroxide extracts the most nicotine, as compared to conventional extraction or pyrolysis. More experiments along this line are planned to further characterize the source of this nicotine.

VI. RESPONSE TO ANALYTICAL REQUESTS

A. **Objective**: To provide analytical support to R&D and Operations personnel and projects.

B. **Results**:

Analyses and investigations by the project personnel during the month of July included:

Several mainstream (MS)/sidestream (SS) samples submitted by H. Randolph were analyzed for glycerin content by capillary gas chromatography. Confirmation of the presence of glycerin in these samples will be made by GC/MS. The results will be reported in a memo.

Several samples of ART stems were analyzed for potassium to confirm accurate application of potassium citrate.

Three filter samples were extracted in methanol and analyzed using capillary GC to determine the amount of triethyl citrate present in the filters. (Project 2305)

Six customer complaint samples were evaluated for contamination.

Ethanol content of foil and cigarettes from the menthol on foil process was determined in order to estimate the environmental loss of ethanol. Initial results indicate little or no loss of ethanol 12 hours after foil application and 12 hours after packing cigarettes.

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